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(54) Title: BLEACHING PROCESS FOR THE PRODUCTION OF HIGH BRIGHT PULPS (57) Abstract A process for the bleaching of mechanical and chemimechanical pulps which includes the steps of treating in a first stage the pulp with a reducing agent and subsequently treating the same pulp with a peroxygen compound in a second stage followed by a subsequent treatment with a peroxygen compound in a third stage.		

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1 BLEACHING PROCESS FOR THE PRODUCTION OF HIGH BRIGHT PULPS

 This invention relates to a multistage bleaching
process in which reducing agents and oxidizing agents
are used sequentially to bleach mechanical and
5 chemimechanical pulps to high brightness levels and
partially remove their yellow shade.

 It is well recognized by those skilled in the art
of mechanical and chemimechanical pulping that the
10 quality of mechanical and chemimechanical pulps need
to be improved in terms of brightness levels, color or
yellowness and rapid reversion characteristics which
occur with yellowing. Therefore various processes are
currently employed in the pulp and paper industry to
15 bleach these pulps for their use in a wide variety of
paper products. The oldest process uses a reducing
agent such as dithionite or sodium and zinc
hydrosulfite (H) to brighten or bleach the pulps. With
this bleaching chemical moderate gains of 4 to 10
20 points are obtained. Maximum brightness levels of 68
to 70% iso can be reached with the addition of
approximately 1% to 1.25% on o.d. pulp of sodium
hydrosulfite. The process is usually carried out in an
aqueous phase at 3 to 5% consistency, a pH of 4.5 to
25 6.0, a temperature of about 60°C and a retention time
of up to one hour. The use of a chelating or
sequestering agent such as sodium tripolyphosphate
(STPP) to remove naturally occurring trace metals is
recommended. This agent is being added to the pulp
30 prior to the addition of the reducing agent or is
incorporated in the bleaching solution.

 Today, peroxide (P) is the most commonly employed
oxidizing agent for bleaching mechanical and
35 chemimechanical pulps. This alkaline process is
normally carried out in a single stage or in a double
stage. In both cases, the bleaching is done at a pulp
consistency of 15 to 35%, moderate temperatures of 50
to 70°C, and retention times of 2 to 3 hours for each

1 stage. In peroxide bleaching, stabilizers such as
sodium silicate and magnesium sulfate are added to the
bleach liquor to prevent decomposition of the
oxidizing agent. Sodium hydroxide is also used to
5 maintain an alkaline pH of 9.5 to 11 so as to increase
the concentration of the perhydroxyl ion OOH^- which is
believed to be the active bleaching agent.
Furthermore, pulps are normally pretreated at low
consistency with organic chelating agents such as
10 sodium diethylenetriamine penta-acetate (DTPA) to
remove naturally occurring trace metals. Additional
quantities are added in the bleach liquor to complex
trace metals that are desorbed from the pulp as a
result of the reaction of the bleaching agents with
15 the chromophores of the pulp. In the bleaching of
commercial pulps, iso brightness of 74-76% are
conventionally achieved using this process with 3%
hydrogen peroxide on o.d. pulp in a single stage while
values of 76-78% iso-brightness are achieved in two
20 stages in which greater retention times and higher
peroxide charge are applied, i.e. 5% hydrogen peroxide
on o.d. pulp.

25 Two stage bleaching of groundwood pulp using
peroxide in the first stage and hydrosulfite
(dithionite) in the second stage is well known and
applied commercially (PH). An ISO-brightness level of
75-77% is achieved. However, much lower brightness
levels are achieved when this two stage sequence is
30 reversed (HP) (Schroter, H., Wbl. Papriefabr. 97, No.
23/24 (1969) p. 1023 and Joyce, P. and Mackie, M.,
CPPA, TAPPI International Pulp Bleaching Conference,
Toronto, Canada, June 11-14, 1979, Preprint Page 116).

35 Other multistage bleaching processes have been
disclosed in the literature but have not found
commercial application. For instance, Loras, V. and
Soteland, N. have published results for a three stage

1 bleaching sequence utilizing borohydride, peroxide and
dithionite sequentially (BPH). This sequence was
reported to yield a brightness of 88% from an initial
level of 67%, an increase of 21 points. (High
5 Brightness Bleaching of Mechanical Pulp, Norsk
Skogindustri, 10/72 p. 255). It is also known from
U.S. Patent 3,100,732 to Smedberg to use a combined
and simultaneous action of an oxidizing agent and a
reducing agent; the patentee also discloses that when
10 using a double stage sequence, one uses the oxidizing
agent first and subsequently the reducing agent.
Liebergott, N., and Heitner, C. disclosed a multistage
process for bleaching high yield and ultra-high yield
pulp in which the pulp is treated sequentially with a
15 peroxygen compound (P), a reducing compound (R) and a
final peroxygen compound (P) to achieve higher
brightness levels (Eur. Pat. Appl. EP 187,477).
Tibbling, P. also disclosed a multiperoxide stage
mechanical pulp bleaching process in which the pulp is
20 treated sequentially with hydrogen peroxide in a first
stage (P) and a second stages (P) and sodium
hydrosulfite in a third stage (H) (Eur. Pat. Appl. EP
191,756). It is claimed that higher brightness levels
are obtained than for those obtained for the bleaching
25 sequence involving hydrogen peroxide (P) followed by
sodium hydrosulfite (H).

It is an object of the present invention to
provide a multistage bleaching process for mechanical
30 and chemimechanical pulps which gives high brightness
levels to such pulps and partially remove their yellow
shade.

According to the present invention, there is
35 provided a method for the bleaching of high yield or
ultra high yield pulp which comprises the steps of
sequentially treating the lignocellulosic fibres with

1 a reducing compound and subsequently treating the same
fibres with peroxide in two successive stages.

5 In greater detail, the method or process includes
three stages where the wood pulp is subjected to
bleaching operations. The wood pulp which may be
utilized is any high yield or ultra yield pulp such as
mechanical, chemimechanical, chemithermomechanical,
groundwood, refiner mechanical pulp, thermomechanical
10 pulp, high yield and ultra high yield sulfite pulps.

In the first stage, the wood pulp is treated with
a reducing compound which may be chosen from many such
reducing compounds known to those skilled in the art.
15 During this first stage, preferred reaction conditions
include:

- (1) a reducing compound charge of about 0.01 to
about 1.5% by weight of oven dried pulp;
- (2) the presence of a chelating agent such as
20 DTPA or STPP;
- (3) a reaction temperature of from about 60°C to
100°C;
- (4) a reaction time of from about 4 to about 120
minutes;
- 25 (5) a pulp consistency of from 3% to about 35%
and
- (6) a reaction terminating pH of about 3.5 to
about 11.0.

30 In the second stage, the pulp is bleached with a
peroxygen compound. Preferred conditions of bleaching
include:

- (1) a peroxygen compound charge of about 0.1% to
about 5% by weight of oven dried pulp in the
35 presence of sodium hydroxide, sodium
silicate, magnesium sulfate and DTPA;
- (2) a reaction temperature of between about 60°C
to about 100°C;

- 1 (3) a reaction time of from about 4 minutes to
 about 180 minutes;
 (4) a pulp consistency of from about 4% to about
 40%; and
5 (5) a reaction terminating pH of from about 8.5
 to about 10.5.

 In the third and final bleaching stage a peroxygen
compound is utilized which is similar to the one used
10 in the second stage. The preferred reaction conditions
include:

- (1) a peroxygen compound charge of about 0.1% to
 about 12.0% in the presence of sodium
 hydroxide, sodium silicate, magnesium sulfate
15 and DTPA;
 (2) a reaction temperature of from about 60°C to
 about 100°C;
 (3) a reaction time of about 4 minutes to about
 240 minutes;
20 (4) a pulp consistency of from about 4% to about
 40%; and
 (5) a reaction terminating pH from about 7.5 to
 about 10.0.

25 The compounds utilized in the process of the
present invention may be selected from among these
well known to those skilled in the art. Thus, the
reducing compounds may be chosen from commercially
inorganic reducing agents such as sodium or zinc
30 hydrosulfite (dithionite), sodium or magnesium
bisulfite, sodium borohydride, Borol* (a solution of
sodium borohydride and sodium hydroxide), thiourea
dioxide, ammonium borohydride, hydrazine and organic
reducing agents such as amine-boranes and phosphine-
35 boranes. It will be noted that some of these reducing
agents are sold commercially with a chelating agent
mixed therewith.

*Registered Trade Mark

1 Examples of the peroxide compound utilized in the
second and third stages may include conventional
inorganic peroxides such as hydrogen and sodium
peroxide and also organic peroxides such as benzyl
5 peroxide, ditertiary-butyl peroxide and peracetic
acid.

 The process flow diagram of figure 1 illustrates
the various steps of a continuous operation in which
10 pulps are bleached in multistage according to the
present invention. In the process the pulp is first
washed with a dewatering device (1) such as, but not
exclusively, a standard screw press, a displacement
washing screw press, a twin wire press, a disc filter
15 or a twin roll press. These devices allow for water
removal from the pulp slurry as well as for washing of
contaminants such as sodium sulfite, metal ions,
organic extractives, dissolved solids, etc., which are
known to impair on the bleaching reactions between the
20 bleaching agents and lignocellulosic fibres. Following
this washing stage the pulp is mixed with the
bleaching liquor containing the reducing agent. Mixing
devices (2) such as single or double shaft mixers,
refiner type mixers, high shear mixers and medium or
25 low consistency pumps can be used. It is important in
this stage of the process to disperse the bleaching
liquor uniformly onto the fibre surface so that
bleaching reactions can prevail over darkening
reactions that also occur when lignocellulosic fibres
30 are submitted to high temperature. After this pulp
mixing stage the reducing agent reacts with the pulp
in an upflow tower or steaming tube (3). A chemical
charge of 0.75 to 1.25% sodium hydrosulfite and of 0.3
to 0.5% of sodium borohydride by weight of oven dried
35 pulp are the preferred charges. A temperature between
65 to 85°C; a consistency between 3.5 to 5% for sodium
hydrosulfite and of 10 to 12% for sodium borohydride;
a reaction time of between 1 to 40 minutes is

1 preferred at this stage to favor a more effective use
of the reducing agent as it cannot be reused in the
system. A reaction terminating pH of about 4.5 to 5.0
for sodium hydrosulfite and of about 10.0 to 10.5 for
5 sodium borohydride is also recommended. Following this
first stage bleaching with a reducing agent the pulp
is dewatered and washed with a dewatering device (4)
such as those described previously and used in
position (1). The purpose is to wash the unreacted
10 reducing agents or byproducts produced from the
bleaching reactions so as to minimize its carry over
to the next bleaching stage. After this pressing and
washing stage the pulp is mixed with the peroxide
bleaching liquor in a mixer (5). Other devices such as
15 those described previously and used in position (2)
can also be used. The efficiency of the mixer is
important at this stage of the process to disperse the
bleaching liquor uniformly onto the fibre surface so
that oxidizing bleaching reactions of the chromophoric
20 groups on the lignocellulosic fibres occur and prevail
over darkening reactions that also occur when pulps
are submitted to high temperatures. We show in figure
1 a mixer (5) which allows for the addition of steam
and the peroxide bleaching liquor simultaneously.
25 Following this mixing stage the pulp is transferred to
a bleaching tower (6). The most preferred charge of
the peroxygen compound in this second stage bleaching
is in amount equal to the charge of the last bleaching
tower or to one third of the charge of the last
30 bleaching tower. Sodium hydroxide, sodium silicate and
magnesium sulfate are preferably added in charge
ranges of 0.5-3.0%, 0.0 to 3.0% and 0.01-0.05%
respectively. It is also preferable to add small
amounts of DTPA between 0.1-0.4%. All these components
35 stabilize the peroxygen compound, in the form of the
perhydroxyl ion, initiate and maintain a stable
bleaching reaction. In a commercial operation the
peroxide bleaching liquor mixed with the pulp at this

1 stage can be either prepared from fresh commercial
components dissolved in water in separate tanks or it
can be a residual bleaching liquor solution from the
last stage bleaching tower (9). We have found from
5 mass balance calculations that this latter is
preferable to minimize the operating and bleaching
cost of the process disclosed in this application. The
size of the second bleaching tower (6) is to be
determined considering the production rate, reaction
10 time and pulp consistency selected or desired. We have
found that a consistency in the 10-12% range, a
retention time of 60 to 90 minutes and a temperature
of 65 to 70°C are preferable to minimize the bleaching
cost of the process disclosed. In figure 1 we show a
15 schematic of a tower which is discharged with a medium
consistency pump so as to have an operation with an
efficient control over the bleaching conditions.

Following this second stage bleaching with an
20 oxidizing agent the pulp is dewatered and washed with
a dewatering device (7) such as those described
previously and used in position (1) and (4). The
purpose is to wash the byproducts produced from the
bleaching reactions which occurred in the second stage
25 bleaching tower, avoid their carry over to the next
bleaching stage and eliminate these from the bleach
plant with an adequate white water recirculation
strategy. After this pressing and washing stage the
pulp is mixed with the peroxide bleaching liquor in a
30 mixer (8). The mixer used and its efficiency are
important at this stage for the same reasons as those
elaborated previously above. Following this mixing
stage the pulp is transferred to a bleaching tower
(9). The preferred charge of the peroxygen compound in
35 this third stage bleaching is 3 to 10% by weight of
oven dried pulps. Sodium hydroxide, sodium silicate
and magnesium sulfate are preferably added in charge
ranges of 0.25-0.3%, 0.01% to 3.0% and 0.01-0.05%

1 respectively. It is also preferable to add small
amounts of DTPA between 0.2-0.4%. In a commercial
operation it is preferable in this last bleaching
stage that fresh peroxide bleaching liquor be used and
5 mixed with the pulp. This bleaching liquor is normally
prepared from fresh commercial components which are
dissolved in water in separate tanks. In addition to
this fresh liquor, a small quantity of the residual
bleaching liquor solution from the same tower (9) can
10 also be used. The residual bleaching liquor is
recovered with the last pair of dewatering presses (11
and 12). We have found that high charges of peroxide
are required in this last bleaching tower to achieve
high brightness levels. The size of the third
15 bleaching tower (9) is to be determined considering
the production rate, reaction time and pulp
consistency selected or desired. We have found that a
consistency in the 20-35% range is preferable to have
high effective concentrations of the oxidizing agents
20 so as to minimize the bleaching cost of the process
disclosed.

In figure 1 we show a schematic of a tower which
is discharged in a transfer chest (10) with a screw
25 conveyer. This device allows for a positive
displacement out of the tower so as to provide an
efficient control over the operating and bleaching
conditions of the pulp in the tower.

30 Following this third stage bleaching with an
oxidizing agent the pulp is washed and dewatered with
dewatering devices, (11) and (12), such as those
described previously. At this stage it is important to
add fresh water in the transfer chest (10) to wash the
35 pulp by dilution and minimize brightness reversion
subsequently. After the final stage of the bleaching
process the pulp is pressed so as to recover the
unreacted peroxide bleaching liquor and to reuse it in

1 the process as shown in figure 1. This white-water
recirculation strategy and counter current washing
lowers the operating cost of the bleaching process
disclosed. The addition of sulfuric acid in the
5 transfer chest (10) or the addition of SO₂ in the
fluffer (13) is also desirable to lower the aqueous
solution pH to about 6 to minimize brightness
reversion subsequently.

Having thus generally described the invention,
10 reference will be made to the following examples;

EXAMPLE 1.

A commercial spruce balsam chemithermomechanical
15 pulp from an Eastern Canadian mill was washed with
0.5% diethylenetriaminepentaacetate (DTPA) for 30
minutes at 60°C and 3% consistency to eliminate metal
ions which impair the bleaching reactions. Following
this treatment, the pulp was pressed to 25%
20 consistency and bleached. The experimental conditions
and chemical charges are given in Table 1.

The bleaching chemicals were mixed by hand with a
20-g pulp sample, while the pulp consistency was
25 simultaneously adjusted with demineralized water.
Subsequently, the bags were sealed and immersed in a
thermostatically controlled bath for the bleaching
reactions to occur. After bleaching, the pulps were
neutralized to destroy the bleaching agents and to
30 adjust the pulp pH to minimize brightness reversion.
For hydrogen peroxide bleaching, sodium metabisulfide
was used, while sulfuric acid was used for the other
bleaching agents.

35 The pulps were neutralized by diluting the pulp to
3% consistency with the neutralizing agent, mixing the
slurry for 5 minutes, and pressing the pulp to 18%
consistency. After neutralization, two samples of 3.5g

1 each were used to make the handsheets. The pulps were
disintegrated for 2 minutes at a consistency of
approximately 0.3%. The sheets were made with
5 demineralized water on a British handsheet machine
following the procedures prescribed by the Canadian
Pulp and Paper Association. The sheets were pressed
for 2 minutes at 50 psig and dried for 24 h at 23°C
and 50% RH. The brightness was measured with an
Elrepho spectrophotometer. Reflectance measurements
10 with Filter Nos. 8, 9, 10, and 11 were made and used
to calculate the color coordinates (CIE LAB) reference
system. ISO brightness reported are the reflectance
values at 457 nm using filter No. 8.

15 In the multistage bleaching experiments, each
stage was similar to the single stage. However, the
two-stage experiments were carried out with 30-g pulp
samples, and 40-g samples were used for three stages.
In all cases, a 7-g sample was taken at the end of
20 each stage and was processed to obtain brightness
values.

The results in Table I show the superiority of the
multistage bleaching process disclosed in the present
25 invention compared to the bleaching processes which
constitute the prior art. High brightness values are
achieved (ISO-brightness and L*) and a great deal of
the yellow shade of the pulps is removed (B* values)
while the pulps have less greenish shade than those
30 bleached with peroxide only (P). These benefits remain
after reversion. It can also be observed that for the
bleaching process disclosed less peroxide is consumed
to achieve higher brightness levels.

1

EXAMPLE 2.

5 A commercial spruce balsam chemithermomechanical pulp was pretreated and bleached following the experimental procedures described in example 1 and under the chemical charges and bleaching conditions given in Table 2. The results in Table 2 show the superiority of the multistage bleaching process disclosed in the present invention compared to other multistage bleaching sequences; peroxide-reducing agent-peroxide (PRP) and peroxide-peroxide-sodium hydrosulfite (PPH). With the sequences sodium hydrosulfite-peroxide-peroxide (HPP) and sodium borohydride-peroxide-peroxide (BPP) higher ISO-brightness values are obtained for a given total peroxide addition level while less peroxide is consumed in the process. Inversely at a constant peroxide consumption level lower ISO-brightness values are obtained with the bleaching procedures of the prior art compared with the process disclosed in this application. In addition to higher brightness values it can be seen from Table 2 that low B* values are obtained which indicate that the pulp bleached following the process disclosed is less yellow than the control pulp, as well as the pulp bleached with hydrogen peroxide only or upon bleaching with the procedures described in the prior art.

30

EXAMPLE 3.

35 A commercial spruce balsam chemithermomechanical pulp was pretreated and bleached following the experimental procedures described in example 1. In this series of experiments the pulp was bleached under different charges of the reducing agent in the first stage. The charges used were from 0.01% to 0.5% while the total peroxide charge was kept constant at 5%. The

1 results in Table 3 show that higher brightness values
are obtained with increasing charges of the reducing
agent. It can be observed that an optimum charge
between 0.1 to 0.3% is desirable. Progressively lower
5 B* values are obtained with the addition of the
reducing agent therefore eliminating a great deal of
the yellowness of the pulp.

10

EXAMPLE 4.

A commercial spruce balsam chemithermomechanical
pulp was pretreated and bleached following the
experimental procedures described in example 1. In
15 this series of experiments the pulp was bleached under
a given charge of 0.3% of the reducing agent, sodium
borohydride, in the first stage while increasing
charges of peroxide up to 5% by weight on oven dried
pulp were added in the second and third stages. The
20 results in Table 4 show that higher brightness values
are obtained with increasing charges of peroxide in
the second and third stages. It can be observed that
small brightness gains are realized with charge levels
slightly in excess of 3% so that preferred conditions
25 would be for an addition level of 4 to 5% in peroxide
o.d. weight when sodium borohydride is used.
Progressively lower B* values are obtained with the
addition of peroxide therefore eliminating a great
deal of the yellowness of the pulp.

30

EXAMPLE 5.

A commercial spruce balsam chemithermomechanical
35 pulp was pretreated and bleached following the
experimental procedures described in example 1. In
this series of experiments the pulp was bleached using
a constant charge of 0.5% sodium hydrosulfite as the

1 reducing agent in the first stage. In the second and
third stages progressively increasing peroxide charges
were added from 1% to 8% o.d. weight o.d. pulp. The
5 results in Table 5 show that higher brightness values
are obtained with increasing charges of peroxide in
the second and third stages. It can be observed that
smooth increases are obtained up to 8% added peroxide
allowing for high brightness levels and appreciable
10 pulp yellowness removal.

EXAMPLE 6.

15 A commercial spruce balsam chemithermomechanical
pulp was pretreated and bleached following the
experimental procedures described in example 1. In
this series of experiments the pulp was bleached using
a constant charge of 1.0% sodium hydrosulfite as the
20 reducing agent in the first stage. In the second and
third stages progressively increasing charges of
peroxide were added from 1% to 8% o.d. weight on pulp.
The results in Table 5 show that higher brightness
values are obtained with increasing charges of
25 peroxide in the second and third stages. It can be
observed that smooth increases are obtained up to 8%
added peroxide allowing for high brightness levels and
appreciable pulp yellowness removal. It can be
appreciated that higher brightness levels are achieved
30 compared to example 5 so that preferred reducing agent
charges are 1.0 to 1.25% o.d. weight on pulp.

35 It will be understood that the above described
embodiments are for purposes of illustration only and
that changes and modifications may be made thereto
without departing from the spirit and scope of the
invention.

TABLE 1:

BLEACHING CHEMICALS AND SEQUENCES

CHEMICAL CHARGES AND BLEACHING CONDITIONS		UNBL. PULP	HYDRO- SULFITE	PEROXIDE	PEROXIDE- HYDROSULFITE		BLEACHING PROCESS DISCLOSED				
			(H)	(P)	(PH)	(PH)	PEROXIDE (PP)	(HPP)	(HPP)	(BPP)	(BPP)
5	FIRST STAGE										
	Na2S103	1	-	3.00	3.00	3.00	3.00	-	-	-	-
	MgSO4	1	-	0.05	0.05	0.05	0.05	-	-	-	-
	NaOH	1	-	3.00	1.60	1.00	1.00	-	-	-	-
	D.T.P.A.	1	0.40	0.40	0.40	0.40	0.40	0.40	0.40	0.40	0.40
	H2O2 ADDED	1	-	3.00	2.50	4.00	2.50	-	-	-	-
	NaBH4	1	-	-	-	-	-	-	-	-	-
	Na2S2O4	1	1.00	-	-	-	-	-	-	0.30	0.30
10	CONSISTENCY	1	5.0	15.0	10.0	10.0	10.0	1.00	1.00	-	-
	TEMPERATURE	C	70	70	70	70	70	5.0	5.0	10.0	10.0
	RETENTION TIME	min.	30	90	90	90	90	30	30	20	20
	pH (INITIAL)	-	5.5	11.0	11.0	11.0	11.0	5.4	5.3	11.7	11.5
	pH (FINAL)	-	5.0	9.6	0.4	0.5	9.5	4.9	5.0	10.4	10.4
	SECOND STAGE										
15	Na2S103	1	-	-	-	-	3.00	3.00	3.00	3.00	3.00
	MgSO4	1	-	-	-	-	0.05	0.05	0.05	0.05	0.05
	NaOH	1	-	-	-	-	1.54	1.74	2.26	1.33	1.33
	D.T.P.A.	1	-	0.40	0.40	0.40	0.40	0.40	0.40	0.40	0.40
	H2O2 ADDED	1	-	-	-	-	2.50	2.50	4.00	1.50	2.50
	Na2S2O4	1	1.00	-	-	-	-	-	-	-	-
	CONSISTENCY	1	5.0	5.0	20.0	10.0	10.0	10.0	10.0	10.0	10.0
	TEMPERATURE	C	70	70	70	70	70	70	70	70	70
	RETENTION TIME	min.	30	30	90	90	90	90	90	90	90
20	pH (INITIAL)	-	5.4	5.4	11.0	10.9	10.8	11.1	11.1	11.0	11.0
	pH (FINAL)	-	4.2	4.4	10.7	0.7	0.0	10.1	10.5	10.5	10.5
	THIRD STAGE										
	Na2S103	1	-	-	-	-	3.00	3.00	3.00	3.00	3.00
	MgSO4	1	-	-	-	-	0.05	0.05	0.05	0.05	0.05
	NaOH	1	-	-	-	-	1.75	2.00	1.00	1.00	1.00
	D.T.P.A.	1	-	0.40	0.40	0.40	0.40	0.40	0.40	0.40	0.40
25	H2O2 ADDED	1	-	-	-	-	2.50	4.00	1.50	2.50	2.50
	CONSISTENCY	1	5.0	5.0	20.0	10.0	10.0	10.0	10.0	10.0	10.0
	TEMPERATURE	C	70	70	70	70	70	70	70	70	70
	RETENTION TIME	min.	30	30	90	90	90	90	90	90	90
	pH (INITIAL)	-	5.4	5.4	11.0	10.9	10.8	11.1	11.1	11.1	11.1
	pH (FINAL)	-	4.2	4.4	10.7	0.7	0.0	10.1	10.5	10.5	10.5
	TOTAL										
30	H2O2 (ADDED)	1	-	3.00	2.50	4.00	5.00	5.00	8.00	3.00	5.00
	H2O2 (RESIDUAL)	1	-	0.79	1.32	2.46	2.18	2.79	5.56	1.66	2.05
	H2O2 (CONSUMED)	1	-	2.21	1.18	1.54	2.82	2.21	2.44	1.34	2.95
	OPTICAL PROPERTIES										
	BEFORE REVERSION :										
35	BRIGHTNESS (ISO-457nm)	1	62.5	68.5	77.1	76.4	77.4	78.5	79.0	80.5	77.6
	L*	-	88.1	91.4	95.1	94.5	94.8	95.3	95.8	95.3	95.1
	A*	-	-0.37	-0.98	-2.16	-1.00	-1.95	-2.66	-1.97	-2.03	-2.67
	B*	-	9.25	9.68	9.16	0.61	0.40	0.33	7.49	6.68	8.35
	AFTER REVERSION :										
	BRIGHTNESS (ISO-457nm)	1	61.9	67.5	75.7	74.5	75.0	76.6	77.7	78.4	76.5
	L*	-	88.0	91.1	94.5	94.2	94.2	94.4	94.6	95.0	94.6
	A*	-	-0.37	-1.14	-3.00	-1.94	-1.75	-3.00	-1.00	-2.01	-2.72
	B*	-	9.64	10.00	9.10	0.40	0.90	7.03	0.00	7.50	0.00

TABLE 2:

BLEACHING CHEMICALS AND SEQUENCE

CHEMICAL CHARGES AND BLEACHING CONDITIONS		UNBL. PULP	BLEACHING PROCESS DISCLOSED												
			(PP)	(PP)	(PBP)	(PBP)	(PHP)	(PHP)	(PPH)	(PPH)	(BPP)	(BPP)	(HPP)	(HPP)	
5	FIRST STAGE														
	Na2SiO3	1	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00	-	-	-	-	
	MgSO4	1	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	-	0.00	-	-	
	NaOH	1	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	-	-	
	D.T.P.A.	1	0.40	0.40	0.40	0.40	0.40	0.40	0.40	0.40	0.40	0.40	0.40	0.40	
	H2O2 ADDED	1	2.50	1.52	2.50	-	2.50	-	2.50	-	-	-	-	-	
	NaBH4	1	-	-	-	-	-	-	-	-	0.30	0.30	-	-	
10	Na2S2O4	1	-	-	-	-	-	-	-	-	-	-	0.50	0.50	
	CONSISTENCY	1	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0	5.0	5.0	
	TEMPERATURE	C	70	70	70	70	70	70	70	70	70	70	70	70	
	RETENTION TIME	min.	90	90	90	90	90	90	90	90	20	20	30	30	
	pH (INITIAL)	-	11.0	11.0	11.0	11.0	11.0	11.0	11.0	11.0	11.5	11.5	5.4	5.2	
	pH (FINAL)	-	9.5	9.5	8.6	8.6	8.4	8.4	8.7	8.7	10.4	10.4	5.2	5.4	
SECOND STAGE															
15	Na2SiO3	1	3.00	3.00	-	-	-	-	3.00	3.00	3.00	3.00	3.00	3.00	
	MgSO4	1	0.05	0.05	-	-	-	-	0.05	0.05	0.05	0.05	0.05	0.05	
	NaOH	1	1.54	1.54	1.00	1.00	-	-	1.70	1.70	1.39	1.39	1.74	1.74	
	D.T.P.A.	1	0.40	0.40	0.40	0.40	0.40	0.40	0.40	0.40	0.40	0.40	0.40	0.40	
	H2O2 ADDED	1	2.50	1.53	-	1.72	-	1.72	2.50	1.85	2.50	2.27	2.50	2.25	
	NaBH4	1	-	-	0.30	0.30	-	-	-	-	-	-	-	-	
	Na2S2O4	1	-	-	-	-	0.50	0.50	-	-	-	-	-	-	
	CONSISTENCY	1	20.0	20.0	10.0	10.0	5.0	5.0	20.0	20.0	10.0	10.0	10.0	10.0	
	TEMPERATURE	C	70	70	70	70	70	70	70	70	70	70	70	70	
20	RETENTION TIME	min.	90	90	20	20	30	30	90	90	90	90	90	90	
	pH (INITIAL)	-	11.0	11.0	12.2	12.2	5.4	5.4	11.0	11.0	11.0	11.0	11.1	11.1	
	pH (FINAL)	-	10.7	10.7	11.0	11.0	4.4	4.4	10.3	10.3	10.5	10.5	0.6	0.6	
THIRD STAGE															
25	Na2SiO3	1	-	-	3.00	3.00	3.00	3.00	-	-	3.00	3.00	3.00	3.00	
	MgSO4	1	-	-	0.05	0.05	0.05	0.05	-	-	0.05	0.05	0.05	0.05	
	NaOH	1	-	-	1.25	1.25	1.00	1.00	-	-	1.00	1.00	1.75	1.75	
	D.T.P.A.	1	-	-	0.40	0.40	0.40	0.40	0.40	0.40	0.40	0.40	0.40	0.40	
	H2O2 ADDED	1	-	-	2.50	1.73	2.50	1.73	-	1.85	2.50	2.50	2.50	2.25	
	Na2S2O4	1	-	-	-	-	-	-	0.50	0.50	-	2.28	-	-	
	CONSISTENCY	1	-	-	20.0	20.0	20.0	20.0	5.0	5.0	20.0	20.0	20.0	20.0	
	TEMPERATURE	C	-	-	70	70	70	70	70	70	70	70	70	70	
	RETENTION TIME	min.	-	-	90	90	90	90	30	30	90	90	90	90	
	pH (INITIAL)	-	-	-	11.0	11.0	11.0	11.0	5.5	5.5	11.1	11.1	11.0	11.0	
	pH (FINAL)	-	-	-	11.0	11.0	9.6	9.6	5.5	5.5	10.5	10.5	10.4	10.4	
30	TOTAL														
	H2O2 (ADDED)	1	5.00	3.05	5.00	3.45	5.00	3.45	5.00	3.70	5.00	4.55	5.00	4.50	
	H2O2 (RESIDUAL)	1	2.10	0.95	2.43	1.45	2.62	1.45	2.57	1.70	2.85	2.55	2.97	2.50	
	H2O2 (CONSUMED)	1	2.90	2.10	2.57	2.00	2.38	2.00	2.43	2.00	2.15	2.00	2.03	2.00	
OPTICAL PROPERTIES															
BEFORE REVERSION :															
35	BRIGHTNESS (ISO-457nm) %	1	62.8	78.5	75.9	79.0	78.9	77.5	76.7	78.0	77.0	78.2	78.2	78.9	
	L*	-	87.3	95.3	94.6	94.9	95.0	94.0	94.7	94.9	94.4	95.0	95.2	95.1	
	A*	-	-0.74	-2.66	-2.60	-1.06	-1.90	-2.02	-1.90	-1.91	-1.75	-2.20	-2.00	-2.00	
	B*	-	0.37	0.33	0.17	0.28	0.10	0.25	0.60	0.79	0.25	0.90	0.02	0.00	
AFTER REVERSION :															
	BRIGHTNESS (ISO-457nm) %	1	61.9	76.6	74.6	77.2	-	75.3	-	76.9	-	77.0	-	78.2	
	L*	-	87.4	94.4	93.0	93.7	-	94.4	-	94.7	-	94.1	-	95.1	
	A*	-	-1.25	-3.00	-3.18	-2.16	-	-1.70	-	-1.95	-	-2.70	-	-1.93	
	B*	-	0.37	0.33	0.17	0.28	-	0.25	-	0.60	-	0.90	-	0.00	

TABLE 3: CHEMICAL CHARGES AND BLEACHING CONDITIONS FOR
THE SEQUENCE SODIUM BOROHYDRIDE-PEROXIDE-PEROXIDE (BPP)

FIRST STAGE								
5	NaOH	%	8.83	8.18	8.17	8.33	1.88	1.67
	D.T.P.A.	%	8.48	8.48	8.48	8.48	8.48	8.48
	NaBH ₄	%	8.81	8.83	8.85	8.18	8.38	8.58
	CONSISTENCY	%	18.8	18.8	18.8	18.8	18.8	18.8
	TEMPERATURE	°C	78	78	78	78	78	78
	RETENTION TIME	min.	28	28	28	28	28	28
	pH (INITIAL)	-	8.3	9.7	18.3	18.9	11.5	11.8
	pH (FINAL)	-	7.8	9.1	9.5	9.8	18.4	11.8
SECOND STAGE								
15	Na ₂ SiO ₃	%	3.88	3.88	3.88	3.88	3.88	3.88
	MgSO ₄	%	8.85	8.85	8.85	8.85	8.85	8.85
	NaOH	%	1.74	2.89	1.56	1.39	1.39	1.22
	D.T.P.A.	%	8.48	8.48	8.48	8.48	8.48	8.48
	H ₂ O ₂ ADDED	%	2.58	2.58	2.58	2.58	2.58	2.58
	CONSISTENCY	%	18.8	18.8	18.8	18.8	18.8	18.8
	TEMPERATURE	°C	78	78	78	78	78	78
	RETENTION TIME	hr.	1.5	1.5	1.5	1.5	1.5	1.5
	pH (INITIAL)	-	11.8	11.8	11.8	11.8	11.8	11.8
	pH (FINAL)	-	9.1	8.8	9.6	9.5	18.5	18.2
THIRD STAGE								
20	Na ₂ SiO ₃	%	3.88	3.88	3.88	3.88	3.88	3.88
	MgSO ₄	%	8.85	8.85	8.85	8.85	8.85	8.85
	NaOH	%	1.25	1.88	8.75	1.25	1.88	1.88
	D.T.P.A.	%	8.48	8.48	8.48	8.48	8.48	8.48
	H ₂ O ₂ ADDED	%	2.58	2.58	2.58	2.58	2.58	2.58
	CONSISTENCY	%	28.8	28.8	28.8	28.8	28.8	28.8
	TEMPERATURE	°C	78	78	78	78	78	78
	RETENTION TIME	hr.	1.5	1.5	1.5	1.5	1.5	1.5
	pH (INITIAL)	-	11.1	11.8	11.8	11.2	11.1	11.8
	pH (FINAL)	-	18.1	18.3	18.4	18.5	18.5	18.6
TOTAL								
25	H ₂ O ₂ (ADDED)	%	5.88	5.88	5.88	5.88	5.88	5.88
	H ₂ O ₂ (RESIDUAL)	%	2.38	2.34	2.41	2.48	2.85	3.19
	H ₂ O ₂ (CONSUMED)	%	2.62	2.66	2.59	2.52	2.15	1.81
OPTICAL PROPERTIES								
BEFORE REVERSION :								
30	BRIGHTNESS (ISO-457nm)%		62.8	77.5	77.2	77.8	78.5	78.2
	L*	-	87.3	95.8	95.8	95.8	95.8	94.6
	A*	-	-8.74	-2.71	-2.75	-2.75	-2.92	-2.28
	B*	-	8.37	8.77	8.54	8.52	8.25	7.98
AFTER REVERSION :								
35	BRIGHTNESS (ISO-457nm)%		61.9	75.9	76.8	76.5	77.8	77.8
	L*	-	87.4	94.1	94.1	94.1	94.1	93.8
	A*	-	-1.25	-3.81	-3.81	-2.49	-2.93	-2.78
	B*	-	8.73	8.19	8.19	7.39	7.39	6.94

TABLE 4: CHEMICAL CHARGES AND BLEACHING CONDITIONS FOR
THE SEQUENCE SODIUM BOROHYDRIDE-PEROXIDE-PEROXIDE (BPP)

FIRST STAGE						
5	NaOH	%	1.00	1.00	1.00	1.00
	D.T.P.A.	%	0.40	0.40	0.40	0.40
	NaBH ₄	%	0.30	0.30	0.30	0.30
	CONSISTENCY	%	10.0	10.0	10.0	10.0
	TEMPERATURE	°C	70	70	70	70
	RETENTION TIME	min.	20	20	20	20
	pH (INITIAL)	-	11.5	11.5	11.7	11.5
	pH (FINAL)	-	10.0	10.3	10.4	10.4
SECOND STAGE						
15	Na ₂ SiO ₃	%	3.00	3.00	3.00	3.00
	MgSO ₄	%	0.05	0.05	0.05	0.05
	NaOH	%	0.70	1.22	1.39	1.39
	D.T.P.A.	%	0.40	0.40	0.40	0.40
	H ₂ O ₂ ADDED	%	0.50	1.00	1.50	2.50
	CONSISTENCY	%	10.0	10.0	10.0	10.0
	TEMPERATURE	°C	70	70	70	70
	RETENTION TIME	hr.	1.5	1.5	1.5	1.5
	pH (INITIAL)	-	11.0	11.0	11.1	11.0
	pH (FINAL)	-	10.0	10.1	10.1	10.5
THIRD STAGE						
20	Na ₂ SiO ₃	%	3.00	3.00	3.00	3.00
	MgSO ₄	%	0.05	0.05	0.05	0.05
	NaOH	%	1.15	1.50	1.00	1.00
	D.T.P.A.	%	0.40	0.40	0.40	0.40
	H ₂ O ₂ ADDED	%	0.50	1.00	1.50	2.50
	CONSISTENCY	%	10.0	10.0	10.0	10.0
	TEMPERATURE	°C	70	70	70	70
	RETENTION TIME	hr.	1.5	1.5	1.5	1.5
	pH (INITIAL)	-	11.1	11.0	11.1	11.1
	pH (FINAL)	-	10.7	10.7	10.5	10.5
TOTAL						
25	H ₂ O ₂ (ADDED)	%	1.00	2.00	3.00	5.00
	H ₂ O ₂ (RESIDUAL)	%	-	0.90	1.66	2.05
	H ₂ O ₂ (CONSUMED)	%	-	1.10	1.34	2.15
OPTICAL PROPERTIES						
BEFORE REVERSION :						
30	BRIGHTNESS (ISO-457nm)%		62.8	74.3	76.9	77.8
	L*	-	87.3	94.2	94.6	95.1
	A*	-	-8.74	-2.42	-2.51	-2.67
	B*	-	8.37	9.48	8.68	8.35
AFTER REVERSION :						
35	BRIGHTNESS (ISO-457nm)%		61.9	73.3	75.1	76.5
	L*	-	87.4	93.5	93.9	94.8
	A*	-	-1.25	-3.01	-2.69	-2.72
	B*	-	8.73	9.20	8.47	8.00

1 **TABLE 5:** CHEMICAL CHARGES AND BLEACHING CONDITIONS FOR
THE SEQUENCE SODIUM HYDROSULFITE-PEROXIDE-PEROXIDE (HPP)

FIRST STAGE							
5	D.T.P.A.	g	0.40	0.40	0.40	0.40	0.40
	Na2S2O4	g	0.50	0.50	0.50	0.50	0.50
	CONSISTENCY	g	5.0	5.0	5.0	5.0	5.0
	TEMPERATURE	C	70	70	70	70	70
	RETENTION TIME	hr.	0.5	0.5	0.5	0.5	0.5
	pH (INITIAL)	-	5.4	5.4	5.5	5.4	5.2
	pH (FINAL)	-	4.8	4.5	4.7	5.2	5.1
10	SECOND STAGE						
	Na2S103	g	3.00	3.00	3.00	3.00	3.00
	HgSO4	g	0.05	0.05	0.05	0.05	0.05
	NaOH	g	0.70	1.22	1.39	1.74	2.09
	D.T.P.A.	g	0.40	0.40	0.40	0.40	0.40
	H2O2 ADDED	g	0.50	1.00	1.50	2.50	4.00
	CONSISTENCY	g	10.0	10.0	10.0	10.0	10.0
	TEMPERATURE	C	70	70	70	70	70
15	RETENTION TIME	hr.	1.5	1.5	1.5	1.5	1.5
	pH (INITIAL)	-	10.9	11.0	11.0	11.1	11.0
	pH (FINAL)	-	9.7	8.7	8.5	8.6	8.8
THIRD STAGE							
20	Na2S103	g	3.00	3.00	3.00	3.00	3.00
	HgSO4	g	0.05	0.05	0.05	0.05	0.05
	NaOH	g	0.75	1.25	1.50	1.75	2.00
	D.T.P.A.	g	0.40	0.40	0.40	0.40	0.40
	H2O2 ADDED	g	0.50	1.00	1.50	2.50	4.00
	CONSISTENCY	g	10.0	10.0	10.0	10.0	10.0
	TEMPERATURE	C	70	70	70	70	70
	RETENTION TIME	hr.	1.5	1.5	1.5	1.5	1.5
	pH (INITIAL)	-	11.0	11.0	11.0	11.0	11.0
	pH (FINAL)	-	10.3	9.8	9.8	10.4	10.0
25	TOTAL						
	H2O2 (ADDED)	g	1.00	2.00	3.00	5.00	8.00
	H2O2 (RESIDUAL)	g	0.26	0.70	1.45	2.97	4.45
	H2O2 (CONSUMED)	g	0.74	1.22	1.55	2.03	3.55
OPTICAL PROPERTIES							
30	BEFORE REVERSION :						
	BRIGHTNESS (ISO-457nm) %		62.5	71.7	75.7	77	78.9
	L*	-	88.1	93.7	94.5	94.9	95.0
	A*	-	-0.37	-1.85	-2.15	-2.31	-2.08
	B*	-	9.25	10.91	9.18	8.87	8.02
	AFTER REVERSION :						
35	BRIGHTNESS (ISO-457nm) %		61.9	71.3	74.7	76.2	78.2
	L*	-	88.0	93.5	94.4	94.7	95.1
	A*	-	-0.37	-2.19	-2.38	-1.81	-1.93
	B*	-	9.64	11.36	9.69	9.06	8.03

TABLE 6: CHEMICAL CHARGES AND BLEACHING CONDITIONS FOR
THE SEQUENCE SODIUM HYDROSULFITE-PEROXIDE-PEROXIDE (HPP)

FIRST STAGE							
5	D.T.P.A.	g	0.40	0.40	0.40	0.40	0.40
	Na2S2O4	g	1.00	1.00	1.00	1.00	1.00
	CONSISTENCY	g	5.0	5.0	5.0	5.0	5.0
	TEMPERATURE	C	70	70	70	70	70
	RETENTION TIME	hr.	0.5	0.5	0.5	0.5	0.5
	pH (INITIAL)	-	5.4	5.5	5.4	5.4	5.3
	pH (FINAL)	-	5.1	5.1	5.0	4.9	5.0
SECOND STAGE							
10	Na2S103	g	3.00	3.00	3.00	3.00	3.00
	MgSO4	g	0.05	0.05	0.05	0.05	0.05
	NaOH	g	1.39	1.39	1.57	1.74	2.26
	D.T.P.A.	g	0.40	0.40	0.40	0.40	0.40
	H2O2 ADDED	g	0.50	1.00	1.50	2.50	4.00
	CONSISTENCY	g	10.0	10.0	10.0	10.0	10.0
15	TEMPERATURE	C	70	70	70	70	70
	RETENTION TIME	hr.	1.5	1.5	1.5	1.5	1.5
	pH (INITIAL)	-	11.1	11.0	11.0	10.9	10.0
	pH (FINAL)	-	9.5	9.1	9.0	8.7	8.0
THIRD STAGE							
20	Na2S103	g	3.00	3.00	3.00	3.00	3.00
	MgSO4	g	0.05	0.05	0.05	0.05	0.05
	NaOH	g	1.00	1.25	1.25	1.75	2.00
	D.T.P.A.	g	0.40	0.40	0.40	0.40	0.40
	H2O2 ADDED	g	0.50	1.00	1.50	2.50	4.00
	CONSISTENCY	g	20.0	20.0	20.0	20.0	20.0
	TEMPERATURE	C	70	70	70	70	70
	RETENTION TIME	hr.	1.5	1.5	1.5	1.5	1.5
25	pH (INITIAL)	-	11.1	11.0	10.9	11.1	11.1
	pH (FINAL)	-	10.2	10.2	9.9	10.5	10.6
TOTAL							
	H2O2 (ADDED)	g	1.00	2.00	3.00	5.00	8.00
	H2O2 (RESIDUAL)	g	0.19	0.81	1.60	2.79	3.56
	H2O2 (CONSUMED)	g	0.81	1.19	1.40	2.21	2.44
OPTICAL PROPERTIES							
BEFORE REVERSION :							
30	BRIGHTNESS (ISO-457nm)%		62.5	71.4	75.7	76.0	79.0
	L*	-	88.1	93.4	94.5	94.5	95.0
	A*	-	-0.37	-2.00	-1.85	-1.66	-1.97
	B*	-	9.25	10.81	9.17	8.45	7.49
AFTER REVERSION :							
35	BRIGHTNESS (ISO-457nm)%		61.9	70.4	74.7	75.7	77.7
	L*	-	88.0	93.1	94.4	94.4	94.8
	A*	-	-0.37	-1.87	-1.93	-1.59	-1.88
	B*	-	9.64	11.04	9.69	8.95	8.00

1 CLAIMS

1. A process for the bleaching of mechanical and chemimechanical pulps which includes the steps of
5 treating in a first stage the pulp with a reducing agent and subsequently treating the same pulp with a peroxygen compound in a second stage followed by a subsequent treatment with a peroxygen compound in a third stage.
- 10 2. The process of claim 1 in which the reducing agent is sodium hydrosulfite.
- 15 3. The process of claim 2 in which treatment of the pulp in the first stage utilizes a chemical charge of
15 0.75 to 1.25% sodium hydrosulfite by weight of oven dried pulp in the presence of a chelating agent at a reaction temperature between 65 to 85°C, a consistency between 3.5 to 5%, a reaction time between 1 and 40 minutes and a reaction terminating pH of about 4.5 to 5.0.
- 20 4. The process of claim 3 in which following the first stage bleaching with a reducing agent the pulp is dewatered and washed to remove unreacted reducing agents and by-products.
- 25 5. The process of claim 4 in which 3 to 10% of peroxygen by weight of oven dried pulp is dispersed into the pulp using a mixer and transferring the pulp and bleaching fluid to a bleaching tower.
- 30 6. The process of claim 5 in which sodium hydroxide, sodium silicate and magnesium sulfate are added to stabilize the peroxygen compound in ranges of 0.5 - 3.0%, 0.0 to 3.0% and 0.01 to 0.05% respectively.
7. The process of claim 6 in which small amounts of DTPA between 0.1 - 0.4% are added to the bleach fluid.

- 1 8. The process of claim 7 in which the consistency of the pulp is in the 10 - 12% range, the temperature is 65 - 70°C and the retention time is 60 to 90 minutes.
- 5 9. The process of claim 8 in which the pulp from the first bleaching tower is dewatered and washed to remove the by-products produced from the bleaching reactions.
- 10 10. The process of claim 9 in which 3 to 10% of peroxygen by weight of oven dried pulp is dispersed into the pulp using a mixer and the pulp and bleaching fluid are transferred to a bleaching tower.
- 15 11. The process of claim 10 in which sodium hydroxide, sodium silicate and magnesium silicate are added to stabilize the peroxygen compound in ranges of 0.5 - 3.0%, 0.0 to 3.0% and 0.01 to 0.05% respectively.
- 20 12. The process of claim 11 in which the consistency of the pulp is in the range from 20 - 35%, and primarily fresh peroxygens are mixed with the pulp.
- 25 13. The process of claim 12 in which the pulp is washed and dewatered following the third stage bleaching.
- 30 14. The process of claim 13 in which sulfuric acid is added to the pulp after washing and dewatering to lower the aqueous solution pH to about 6.
- 35 15. The process of claim 1 in which the reducing agent is sodium borohydride.
16. The process of claim 15 in which treatment of the pulp in the first stage utilizes a chemical charge of 0.3 to 0.5% of sodium borohydride by weight of oven dried pulp in the presence of a chelating agent at a reaction temperature between 65 to 85°C, a consistency between 10 and 12%, a reaction time between 1 to 40 minutes and a reaction terminating pH of 10.0 to 10.5.

1 17. The process of claim 16 in which following the
first stage bleaching with a reducing agent the pulp is
dewatered and washed to remove unreacted reducing agents
and by-products.

5 18. The process of claim 17 in which 3 to 10% of
peroxygen by weight of oven dried pulp is dispersed into
the pulp using a mixer and transferring the pulp and
bleaching fluid to a bleaching tower.

10 19. The process of claim 18 in which sodium hydroxide,
sodium silicate and magnesium sulfate are added to
stabilize the peroxygen compound in ranges of 0.5 - 3.0%,
0.0 to 3.0% and 0.01 to 0.05% respectively.

15 20. The process of claim 19 in which small amounts of
DTPA between 0.1 - 0.4% are added to the bleach fluid.

20 21. The process of claim 20 in which the consistency
of the pulp is in the 10 - 12% range, the temperature is
65 - 70°C and the retention time is 60 to 90 minutes.

25 22. The process of claim 21 in which the pulp from the
second stage bleaching tower is dewatered and washed to
remove the by-products produced from the bleaching
reactions.

30 23. The process of claim 22 in which 3 to 10% of
peroxygen by weight of oven dried pulp is dispersed into
the pulp using a mixer and the pulp and bleaching fluid
are transferred to a bleaching tower.

35 24. The process of claim 23 in which sodium hydroxide,
sodium silicate and magnesium silicate are added to
stabilize the peroxygen compound in ranges of 0.5 - 3.0%,
0.0 to 3.0% and 0.01 to 0.05% respectively.

25. The process of claim 24 in which the consistency
of the pulp is in the range from 20 - 35%, and primarily
fresh peroxygens are mixed with the pulp.

1 26. The process of claim 25 in which the pulp is
washed and dewatered following the third stage bleaching.

5 27. The process of claim 26 in which sulfuric acid is
added to the pulp after washing and dewatering to lower
the aqueous solution pH to about 6.

10 28. The process of claim 1 characterized by the
reducing compound being selected from the group
consisting of sodium bisulfite, magnesium bisulfite, zinc
hydrosulfite, BOROL, thiurea dioxide, ammonium
borohydride and hydrazine.

15 29. The process of claim 1 in which the treatment of
the pulp with the reducing agent utilizes a charge of
about 0.01 to about 1.5% by weight in the presence of a
chelating agent at a reaction temperature of between 60°C
to 100°C for a time of between 4 to 120 minutes at a pulp
consistency of from 3% to 35% and a reaction terminating
20 pH of between 3.5 to about 11.0; the process being
further characterized by washing said pulp after
treatment.

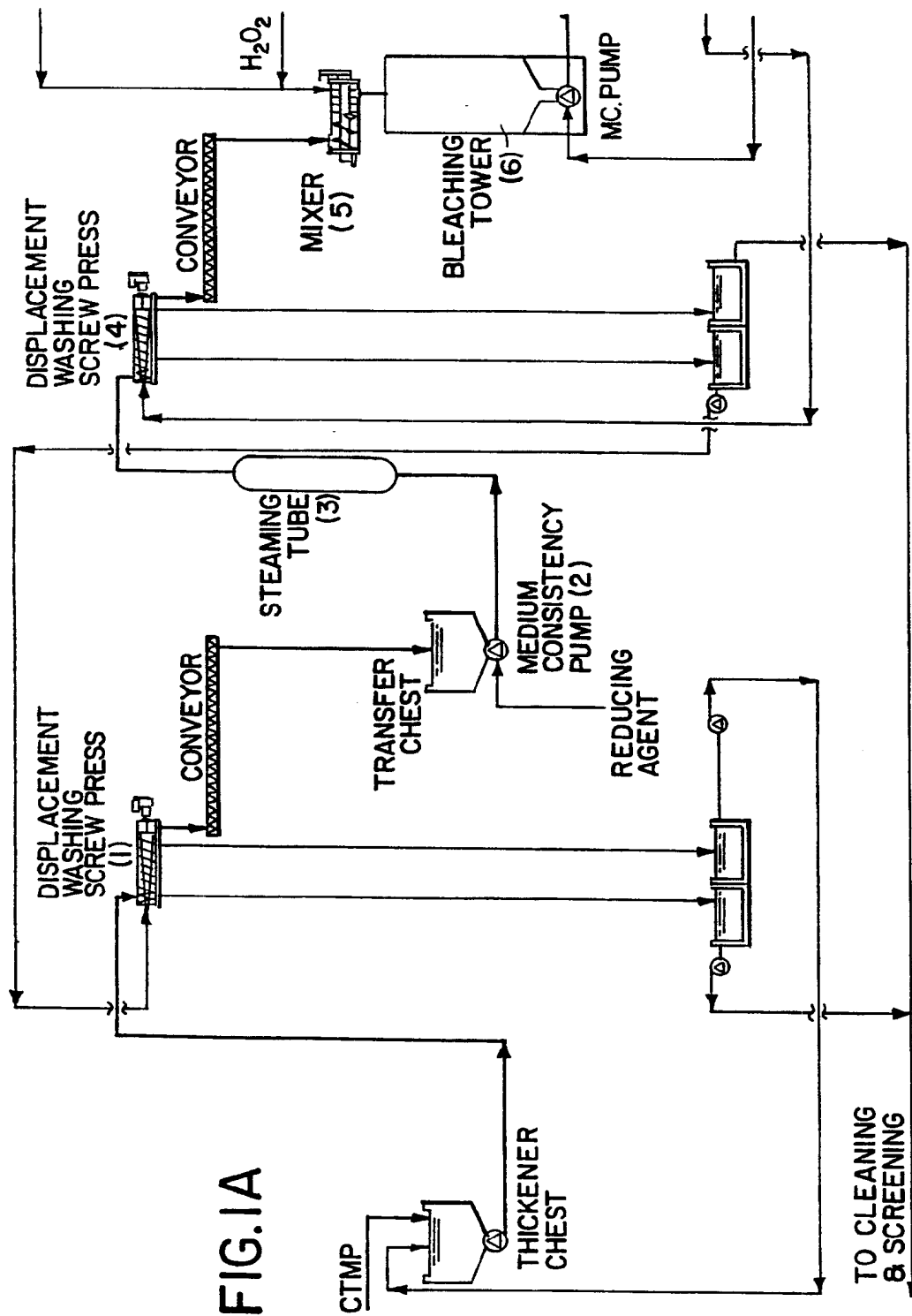
25 30. The process of claim 29 characterized by the
peroxygen compound being selected from the group
consisting of hydrogen peroxide, sodium peroxide, benzyl
peroxide, ditertiarybutyl peroxide and peracetic acid.

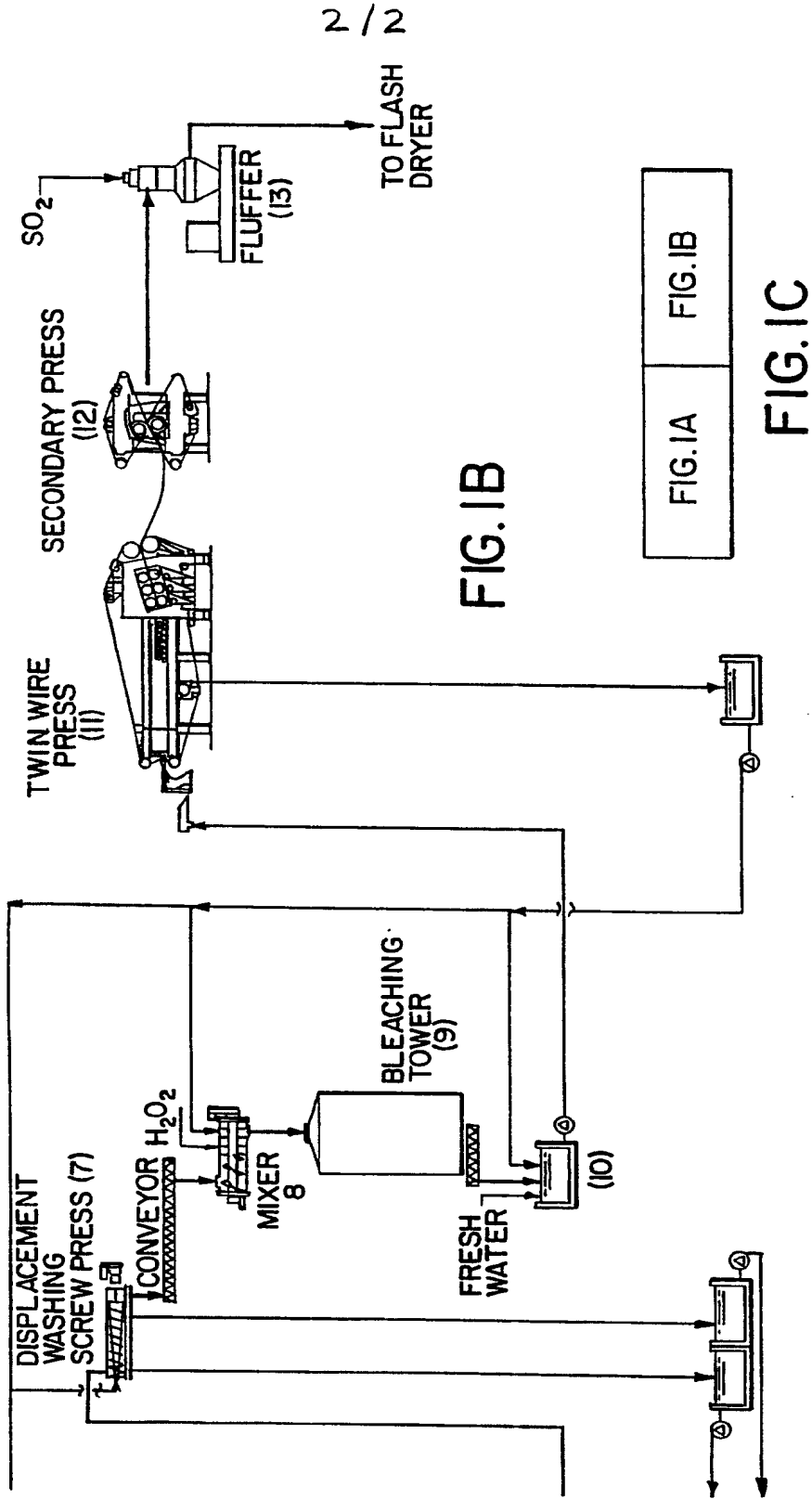
30 31. The process of claim 30 in which the treatment of
the pulp with a peroxygen compound in the second stage
utilizes a charge of between 0.01% to about 5.0% by
weight at a temperature of between 60°C to 100°C for a
time period of between 4 minutes to 180 minutes at a pulp
consistency of between 4% to about 40% and a reaction
35 terminating pH of between 0.5 to 10.5.

32. The process of claim 31 in which the treatment
with said peroxygen compound in the third stage utilizes
a charge of between 0.1 to about 12% by weight based on
oven dried pulp at a temperature of between 60°C to 100°C

- 1 for a period of from 4 minutes to 250 minutes at a pulp
consistency of between 4% and 40% and a reaction
terminating pH of from 7.5 to about 10.0.
- 5 33. The process of claim 32 characterized by the
peroxygen compounds being selected from the group
consisting of sodium peroxide, benzyl peroxide,
ditertiarybutyl peroxide and peracetic acid.
- 10 34. The process of claim 33 characterized by the
treatment of the pulp with the peroxygen compounds being
carried out in the presence of sodium hydroxide, sodium
silicate, magnesium sulfate and DTPA.
- 15 35. The process of claim 1 characterized by the pulp
being selected from the group of pulps consisting of high
yield and ultra high yield pulps which are referred to as
mechanical, chemimechanical, chemithermomechanical,
groundwood, high-yield or ultra high yield sulfite pulps.

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INTERNATIONAL SEARCH REPORT

International Application No

PCT/CA 90/00097

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶		
According to International Patent Classification (IPC) or to both National Classification and IPC ⁷ Int.Cl. 5 D21C9/10		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
Int.Cl. 5	D21C	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸		
III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹		
Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
Y	EP,A,0187477 (PULP AND PAPER RESEARCH INSTITUTE OF CANADA) 16 July 1986 see the whole document (cited in the application) ---	1-11, 14-24, 27-35
Y	BULLETIN OF THE INSTITUTE OF PAPER CHEMISTRY. vol. 53, no. 2, August 1982, APPLETON US page 260 M.YOTSUYA et al.: "Peroxide bleaching of high-yield pulp." see the whole document ---	1-11, 14-24, 27-35
A	EP,A,0191756 (KAMYR AB) 20 August 1986 see the whole document (cited in the application) ---	
¹⁰ Special categories of cited documents: ¹⁰ "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "I" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. "&" document member of the same patent family		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
20 JULY 1990	16 AUG 1990	
International Searching Authority	Signature of Authorized Officer	
EUROPEAN PATENT OFFICE	SONGY O.M-L.A. 	

Form PCT/ISA/210 (second sheet) (January 1985)

**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO.**

CA 90/00097
SA 35818

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent Office EDP file on
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20/07/90

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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		US-A- 4804440	14-02-89
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		SE-A- 8600615	16-08-86
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For more details about this annex : see Official Journal of the European Patent Office, Nr. 12/82

